Study of Crystal Structure Profile Fitting of CuO for different Intensities of Gamma Radiation using Rietveld Refinement Method

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Abstract— *The study of crystal structure profile fitting described by Hugo Rietveld named Rietveld Refinement became popular for profile fitting and microstructural analysis. The Rietveld method refines user-selected parameters to minimize the difference between an experimental parameter (observed data) and a model based on the hypothesized crystal structure and instrumental parameters (calculated data). In this paper, profile fitting of CuO has been discussed for different intensities of XRD data. Here Goodness of fitting is kept 1-2. For different dose the goodness of fitting changes.*

Keywords— CuO, Powder diffraction, gamma radiation.

I. INTRODUCTION

1.1 Cupric Oxide (CuO)

During the past few years, the nano-semiconductors have proved itself beside the bulk semiconductors and have attracted extensive attention from scientists not only for the dramatic changing of their properties as a function of size, which is so significant for fundamental research, but also for their applications in different topics of technology as nano-electronics, photonics, optoelectronics, nano- medicine and nano-devices of renewable energy. It is well recognized that metal oxides have reached an important place in several areas of chemistry, physics and materials science. Currently, copper oxides, especially found a wide application domain in catalytic, field emissions, gas sensing, lithium batteries, and solar cells [2–6].

Metal oxide semiconductor thin films have been studied for their use in optoelectronic and photonics technology. Among the metal oxides, copper oxide (CuO) is a p-type semiconducting oxide material. CuO exhibits superior properties, including a direct band gap (~ 1.2 eV-2.1 eV), non-toxic nature, excellent chemical stability, cost effective synthesis, abundance in nature and reasonably good electrical properties [7-9]. CuO has received considerable attention for various applications, including gas sensors, biosensors, solar cells, batteries, magnetic storage materials, catalysts, diodes and transistors [8-12].

Interaction of radiant energy with matter, especially y–radiation, is an enormously important from the view point of theory and practice. Gamma irradiation, the high energetic form of electromagnetic wave, causes two effects when interacting with materials: first, ionization which creates secondary reactions with ejected electrons and second, the atomic displacement which defects into atomic lattice. Irradiation of solids with high energy radiation, like y- rays, electrons or neutrons expected to affect their optical, electrical and physical properties. The various researches illustrate that when solid state materials are exposed to ionizing radiation, their microstructural properties are altered. Numerous efforts have recently been made to investigate the influence of gamma radiation on different metal oxides and polymers. Copper Oxide is a group II-VI semiconductor with optical properties. It exhibits a wide variety of morphologies in the nano regime that can be grown by tuning the growth habit of the CuO crystal. There are two stable crystalline phases of the Copper oxide such as Cupric oxide (CuO) or tenorite and Cuprous oxide (Cu2O) or cuprite.

1.2 Crystal Structure Analysis

A crystal with its strictly periodic atomic structure represents a natural, very symmetrical three- dimensional diffraction grating for wavelengths of the order of the interatomic distances. Crystal structure analysis is thus based on the theories of symmetry (space groups) on the one hand and of interaction of radiation with solids (diffraction) on the other. The diffraction techniques, with the help of extensive computer calculations, lead to the atomic arrangements of crystalline materials. Depending on the problem, X-rays, electrons, or neutrons are used, which provide the electron-density, electrostatic potential density and nuclear density (also magnetic spin density) distribution, respectively, in a crystal[13].

All possible arrangements of atoms in crystals are governed by the 230 types of space groups, derived in 1890 by the crystallographer E.S. Fedorov and the mathematician A. Schoen flies. X-ray diffraction of crystals was discovered by the physicists M. Von Laue, W. Friedrich, and P. Knipping in 1912. In 1913- 1914, W.H. Bragg and W.L. Bragg first applied X-ray diffraction to the experimental confirmation of the structures of single crystals of NaCl, Cu, diamond, etc. previously predicted by W. Barlow. The application of X-ray diffraction was extended to polycrystalline materials in 1916 by P. Debye and P. Sherrer. Details of the history of crystallography can be found in a recent Historical Atlas by 1. Lima-de-Faria.

The power of a structure analysis of a synthetic crystal or a mineral and the reliability and accuracy of the results depend on many factors: sample quality, radiation source, apparatus and techniques available, especially for the measurement of the diffracted intensities. The first problem of a structural study is the determination of the symmetry and the lattice parameters of the crystal. The next step is the derivation of an atomic model. The structure is then refined from the diffraction data, taking into account the finer effects of the interaction between sample and radiation. The final stage is the crystallochemical analysis which comprises interpretation of the geometrical model, calculation of interatomic distances, valency angles, sizes, and orientations of thermal-motion ellipsoids and, finally, generation of visible structure models on a display or a plotter.

Further advances of the theory and the methods of structure analysis provide information not only on the geometry but also on more subtle features of the mineral structure, such as isomorphous replacement, disorder, variable atomic occupation of crystallographic sites, sizes and misorientation of mosaic blocks in single crystals, as well as thermal motion of the atoms including its anisotropy[13].

1.3 X-ray Powder Diffraction

Powder diffraction is a scientific technique using X-ray, neutron, or electron diffraction on powder or microcrystalline samples for structural characterization of materials. An instrument dedicated to performing such powder measurements is called a powder diffractometer. X-ray powder diffraction (XRD) is a rapid analytical technique primarily used for phase identification of a crystalline material and can provide information on unit cell dimensions.

Max von Laue, in 1912, discovered that crystalline substances act as three- dimensional diffraction gratings for X-ray wavelengths similar to the spacing of planes in a crystal lattice. X-ray diffraction is now a common technique for the study of crystal structures and atomic spacing.

X-ray diffraction is based on constructive interference of monochromatic X-rays and a crystalline sample. These X-rays are generated by a cathode ray tube, filtered to produce monochromatic radiation, collimated to concentrate, and directed toward the sample. The interaction of the incident rays with the sample produces constructive interference (and a diffracted ray) when conditions satisfy Bragg's Law ($n\lambda=2d \sin \theta$). This law relates the wavelength of electromagnetic radiation to the diffraction angle and the lattice spacing in a crystalline sample. These diffracted X-rays are then detected, processed and counted. By scanning the sample through a range of 2θ angles, all possible diffraction directions of the lattice should be attained due to the random orientation of the powdered material. Conversion of the diffraction peaks to d- spacing allows identification of the mineral because each mineral has a set of unique d-spacing. Typically, this is achieved by comparison of d-spacing with standard reference patterns.

1.4 Rietveld Refinement

Rietveld refinement is a technique described by Hugo Rietveld for use in the characterization of crystalline materials. The neutron and x-ray diffraction of powder samples results in a pattern characterized by reflections (peaks in intensity) at certain positions. The height, width and position of these reflections can be used to determine many aspects of the material's structure.

The Rietveld method uses a least-squares approach to refine a theoretical line profile until it matches the measured profile. The introduction of this technique was a significant step forward in the diffraction analysis of powder samples as, unlike other techniques at that time; it was able to deal reliably with strongly overlapping reflections.

The method was first implemented in 1967 and reported in 1969 for the diffraction of monochromatic neutrons where the reflection-position is reported in terms of the Bragg angle 2θ. This terminology will be used here although the technique is equally applicable to alternative scales such as x-ray energy or neutron time-of-flight. [16]

The Rietveld method refines user-selected parameters to minimize the difference between an experimental pattern (observed data) and a model based on the hypothesized crystal structure and instrumental parameters (calculated pattern) [17].

The Rietveld method use the most physically-accurate model available for the intensities (the structure factor equation including iso or anisotropic thermal parameters, multiplicity, Lorentz and polarization factors, preferred orientation, absorption, extinction, anomalous scattering, etc.) but uses a phenomenological description of peak shapes (including both instrumental or micro-structural factors affecting peak-shapes), and a physically sense-less background representation. Some of the corrections of the intensities (e.g. absorption) are not exact, though, they come from approximate models, but perform well when the effect of this factor is not very significant (and sometimes they are the only available model). Related methods used for determining intensities use the non- intensity-related parameters used in the Rietveld formula, to extract intensities from the fit.

The Rietveld Method, using an accurate representation of the intensities, performs well for structural analysis (refinement of structural model) and also quantitative phase analysis since relative intensities are correctly accounted for even in the presence of preferred orientation, micro-absorption, etc. that can be reasonably corrected with some physically-sensible models. Rietveld method as crystal structure refinement method is a method to check, how close to reality your guess is and to refine it so that the residual functions mentioned above will become as low as possible [18].

1.5 Full Prof Suite

The FullProf Suite (for Windows, Linux and macOS) is formed by a set of crystallographic programs (FullProf, WinPLOTR, EdPCR, GFourier, etc...) mainly developed for Rietveld analysis (structure profile refinement) of neutron (constant wavelength, time of flight, nuclear and magnetic scattering) or X-ray powder diffraction data collected at constant or variable step in scattering angle 2theta.The different programs can be run either in standalone form (from a console window or clicking directly in a shortcut) or from the interfaces WinPLOTR and/or EdPCR.

The programs within the FullProf Suite are distributed in the hope that they will be useful, but without any Warranty of being free of internal errors. In no event will the authors (or their institutions) be liable to you for damages, including any general, special, incidental or consequential damages arising out of the use or inability to use the programs (including but not limited to loss of data or data being rendered inaccurate or losses sustained by you or third parties or a failure of the program to operate with any other programs). The authors are not responsible for erroneous results obtained with the programs.

The first versions of the program FullProf were based on the code of the DBWS program which was also a major modification of the original Rietveld-Hewat program. The program FullProf has been re-written using the full capabilities of the new Fortran 95 standard during

1997-1998. It is progressively being transformed in a program based in the Crystallographic Fortran 95 Modules Library [3]. The program works with some allocatable arrays so the user can directly control the dimensions of important arrays at run time. In this paper we shall describe some elementary points concerning the methods implemented in the program and how to use it. For further details the user should consult the manual and tutorials. The Windows version of the program and all the suite of programs related to FullProf are now distributed within the FullProf suite installer (setup_FullProf_Suite.exe). This installer, additional documents and tutorials, can be found in the FullProf Web site [19-20]

II. EXPERIMENTAL PART

2.1 Preparation of XRD data file

Here CuO powder is taken. Cu at wavelength 1.540560 A° is taken. The data taken here is 2Θ. Initial theta value 25.00 final 2 theta value 80.00 and step used here the default step, i.e. 0.02.

2.2 Creating PCR file

XRD data file is taken in Microsoft .xlsx file. From that data file a .dat file is created to perform the operation. To develop the pcr file crystallographic information file is taken from crystallography open database for CuO. 12- Coefficient Fourier Cosine series is taken for background type. Phase of CuO is monoclinic and space group is C 2/c.

Rietveld refinement, profile matching and integrated intensity refinement of X- ray data was performed by using FullProf Suite Program. The pseudo-voigt function was used to refine CuO x-ray data applying C 2/c space group and monoclinic symmetry with Lau class 2 /m. The parameters thus obtained for the atomic positions of Cu and O element are presented in Table 1. Other parameters for example, full width at half maximum (FWHM), shape parameters, linear interpolations etc. were refined iteratively. All the diffraction peaks could be suitably indexed to the CuO teronite phase [13–15]. Refinement results reveal a monoclinic lattice structure (JCPDS 141–0254), having lattice constants a = 4.67910 Å, b = 3.48050 Å and c = 5.11830 Å along with $\alpha = \gamma = 90°$, and $\beta = 98.5981°$.

TABLE 1
RIETVELD REFINEMENT PARAMETERS USED FOR ATOMIC POSITIONS IN FULLPROF SUITE PROGRAM

Elements			x	y	z	Occ.	B
Atom#1	Cu	Cu	0.25000	0.25000	0.00000	1.000	1.00
Atom#2	O	O	0.00000	0.41840	0.25000	1.000	1.00

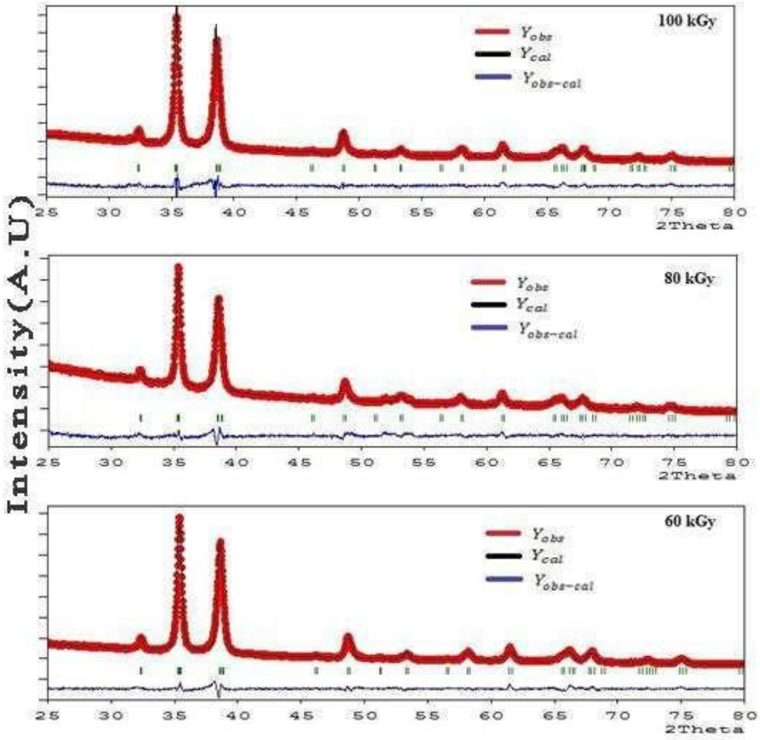

FIGURE 1: Refined output graph for different intensities (60 KGy, 80 KGy, 100 KGy)

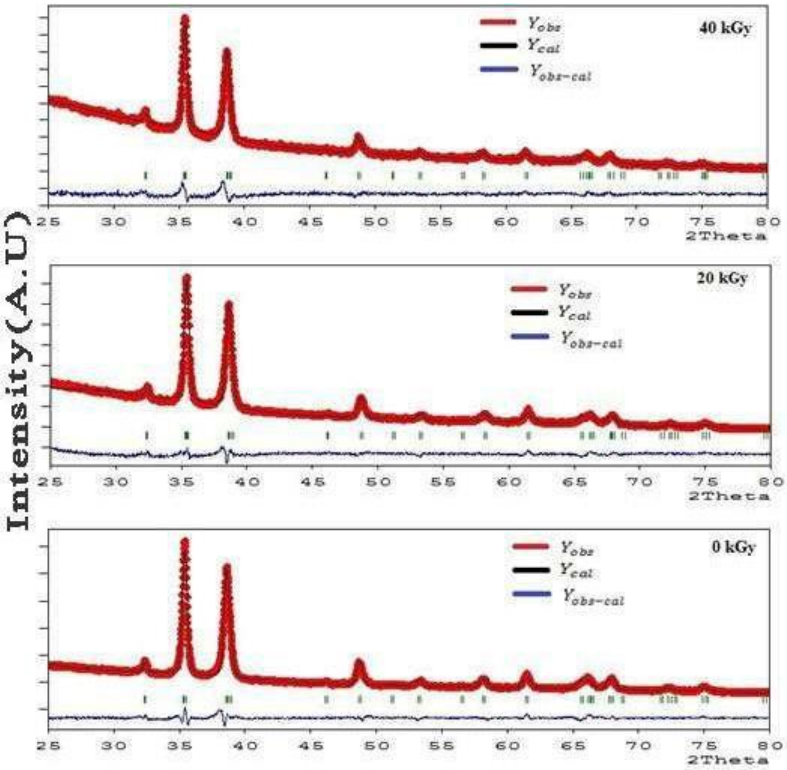

FIGURE 2: Refined output graph for different intensities (0 KGy, 20 KGy, 40 KGy)

2.3 Profile fitting

Here background points are refined first. Then instrumental components were refined. Profile and atomic positions were refined for the final step. In FWHM section U, V, W was refined first. And IG parameter is refined at the last step to get good fitting. All parameters were refined one by one first. Then Several Parameters were refined for various combinations of sequences to get good profile fitting.

The refined parameters are given in table-2**:**

TABLE 2
REFINED PARAMETERS

Dose (kGy)	Lattice Parameter	R_p	R_{wp}	R_{esp}	GOF	X^2	$R_{Bra g}$	R_F	Cell Volume
0	a = 4.67865 b = 3.42799 c = 5.12931 β = 99.3642	18.8	13.3	8.53	1.56	2.45	4.12	3.70	81.166
20	a = 4.67950 b = 3.43057 c = 5.12791 β = 99.3910	23.9	16.1	11.14	1.45	2.09	7.88	6.21	81.217
40	a = 4.68230 b = 3.42301 c = 5.12750 β = 99.4527	36.2	21.5	17.25	1.25	1.55	7.56	4.37	81.065
60	a = 4.68080 b = 3.42870 c = 5.12930 β = 99.3620	15.2	11.4	7.18	1.59	2.53	3.17	3.50	81.224
80	a = 4.70150 b = 3.44830 c = 5.15670 β = 99.3620	27.1	16.4	12.29	1.33	1.78	7.29	5.59	82.489
100	a =4.67990 b = 3.42751 c = 5.12401 β =99.3811	21	14.8	9.76	1.52	2.31	4.47	3.54	81.092

III. RESULT AND DISCUSSION

3.1 Lattice constant

Lattice constant, or lattice parameter, refers to the physical dimension of unit cells in a crystal lattice. Lattices in three dimensions generally have three lattice constants, referred to as a, b, and c. However, in the special case of cubic crystal structures, all of the constants are equal and we only refer to a. Similarly, in hexagonal crystal structure, then a and b constants are equal, and we only refer to the and c constants. For monoclinic a, b, c are different. α, γ are 90º and β is different. A group of lattice constants could be referred to as lattice parameters. However, the full set of lattice parameters consist of the three lattice constants and the three angles between them [21].

3.2 Cell volume

The volume of the unit cell can be calculated from the lattice constant lengths and angles. If the unit cell sides are represented as vectors, then the volume is the dot product of one vector with the cross product of the other two vectors. The volume is represented by the letter V[21]. For the general unit cell.

$$V=abc\sqrt{}(1 + 2\cos\alpha\cos\text{þ}\cos y - \cos^2\alpha - \cos^2\text{þ} - \cos^2 y)$$

For monoclinic lattices with $\alpha = 90°$, $\gamma = 90°$, this simplifies to

$$V = abc\sin\beta$$

For orthorhombic, tetragonal and cubic lattices with $\beta = 90°$ as well, then V = abc.

For intensity 40 kGy unit cell volume is lowest, 81.065 A °. For 80kGy cell volume is highest, 82.489.

3.3 R factors

Weighted sum of squares WSS = $\sum_{i=1}^{N}[w_i(I_i^{exp} - I_I^{cal}]^2$

Where

$$wi = \frac{1}{\sqrt{(Ii^{\exp})}}$$

R structure factor: $R_f = \frac{\sum \left|(I_k^{obs})^{\frac{1}{2}} - (I_k^{ca})^{\frac{1}{2}}\right|}{\sum (I_k^{obs})^{\frac{1}{2}}}$ where I_k is the intensity of K^{th} reflection at the end of refinement cycle.

R Bragg factor: $R_{Bragg} = \frac{\sum \left|(I_k^{obs} - I_k^{cal})\right|}{\sum I_k^{obs}}$

R weighted pattern: $R_{wp} = [\frac{\sum [w_i(y_i^{obs} - yi^{cal})^2}{\sum w_i(y_i^{obs})^2}]^{1/2}$ where $y_i =$ gross intensity at I^{th} step

Goodness of fit: $\frac{R_{wp}}{\mathrm{R}_{\exp}}$

$$X^2 = (\frac{R_{wp}}{R_{\exp}})^2$$

$R_{\exp} = [\mathrm{N} - \mathrm{P})/\sum w_i (y_i^{obs})^2]^{1/2}$ where $N =$ Number of points, $P =$ number of parameters [22]

IV. CONCLUSION

Materials are essential to our technological society: Semiconductors in the electronic industry, zeolites as catalysts in the petrochemical industry, ceramics in medicine and engineering and possibly in the future, high –temperature superconductors in electrical engineering.

In order to understand the properties of these materials and to improve them, the

Atomic structure has to be known. An effective way to do this is by means of diffraction techniques using neutrons from nuclear reactors and particle accelerators or X-rays from X-ray tubes and synchrotrons. The Single crystal diffraction technique using relatively large crystal of the material, gives a set of separate data from which the structure can be obtained.

However, most materials of technical interest cannot grow large crystals, so one has to resort to the powder diffraction technique using material in the form of very small crystallites. The drawback of this conventional powder method is that the diffraction peaks grossly overlap, thereby preventing proper determination of the structure. The" Rietveld Method" creates a virtual separation of these overlapping peaks, thereby allowing an accurate determination of the structure .The method has been so successful that nowadays the structure of materials, in the form of powders, is routinely being determined, nearly as accurately as the results obtained by single crystal diffraction techniques. An even more widely used application of the method is in determining the components of chemical mixtures. This quantitative phase analysis is now routinely used in industries ranging from cement factories to the oil industry.

V. FUTURE WORK

Our aim is to lesson to the difference the calculated value of R factor and the expected value of R factor. If the difference is less, the structure of new compound will be more accurate. Then we easily characterize the new compound. The difference can be lessening using linear background. Crystallite size, strain and microstructure analysis of CuO may be done in future.

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